Photocatalysis of aqueous perfluorooctanoic acid by TiO_2 and Ga_2O_3 assisted with peroxymonosulfate under UV and visible light

By

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Certificate of original authorship

I, Bentuo Xu, declare that this thesis, is submitted in fulfilment of the requirements for the award of PhD, in the FEIT at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

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Finally, I am indebted to all my family and friends their unconditional support and encouragement.

Dedication

This thesis is deeply dedicated to the following people:

To my lovely parents

Xiuru Xu

&

Xiaowei Chen

For their unconditional support, enthusiastic encouragement

and endless love

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Table 5-1

The key experimental parameters and their values in this study.

Table 6-1

Comparison of Photocatalytic conditions for PFOA removal by TiO_2/PMS in this study and other catalysts in previous literatures.

Table 7-1

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Abbreviations

Bismuth oxychloride = BiOCl

Benzoquinone = BQ

Bismuth sulfide = Bi_2S_3

Carbon-fluorine = C-F

Carbon nitride = C_3N_4

Cerium dioxide = CeO_2

Cadmium sulfide = CdS

Disodium ethylenediaminetetraacetate = EDTA-Na_2

Dissolved organic matter = DOM

Dissolved oxygen = DO

Dry weight = dw

Gallium oxide = Ga_2O_3

Perchloric acid = $HClO_4$

Porous nanoplates = PNPs

Indium trioxide = In_2O_3

Membrane bioreactor = MBR

Multiple reaction monitoring = MRM

Nanoporous nanospheres = NPNs

Nanoplates = NPs

Hydroxyl radicals = •OH

Perfluoroalkyl substances = PFAS

Perfluorobutanoic acid = PFBA

Perfluorocarboxylic acids = PFCA

Perfluoroheptanoic acid = PFHpA

Perfluorohexanoic acid = PFHxA

Perfluorooctanoic acid = PFOA

Perfluorooctane sulfonic acid = PFOS

Perfluoropentanoic acid = PFPeA

Peroxymonosulfate = PMS

Relative standard deviation = RSD

Scanning electron microscope = SEM

tert-butyl alcohol = TBA

tert-butanol = *t*-BuOH

Trifluoroacetic acid = TFA

Titanium dioxide = TiO_2

Titanate nanotubes (TNTs)

Total organic carbon = TOC

Multiwall carbon nanotube = MWCNT

Wet weight = ww

Wastewater treatment plant = WWTP

X-ray diffraction = XRD

Zinc oxide = ZnO

Nomenclatures

E_g = optical band edge

Φ = quantum yield

pH_{PZC} = zero charge

C_0 = initial concentration

C_t = concentration at min *t*

k = rate constant

k_f = the fluence-based first-order rate constant

$\tau_{1/2}$ = half-life

O_3 = ozonation

hv = photon

C-F = carbon-fluorine

$SO_4^{\bullet-}$ = sulfate radicals

h^+ = hole

e^- = electron

F^- = fluorine ion

List of publications

1st author journal articles:

(1). ***Bentuo Xu**, Mohammad B. Ahmed, John L. Zhou, Ali Altaee. Visible and UV photocatalysis of aqueous perfluorooctanoic acid by TiO_2 and peroxymonosulfate: Process kinetics and mechanistic insights. ***Chemosphere*** 243 (2020) 125366.

(2). ***Bentuo Xu**, John L. Zhou, Ali Altaee, Mohammad B. Ahmed, Md Abu Hasan Johir, Jiawei Ren, Xiaowei Li. Improved photocatalysis of perfluorooctanoic acid in water by Ga_2O_3/UV system assisted by peroxymonosulfate. ***Chemosphere*** 239 (2020) 124722.

(3). ***Bentuo Xu**, Mohammad Boshir Ahmed, John L. Zhou, Ali Altaee, Minghong Wu, Gang Xu. Graphitic carbon nitride based nanocomposites for the photocatalysis of organic contaminants under visible irradiation: progress, limitations and future directions. ***Science of the Total Environment*** 633 (2018) 546-599.

(4). **Bentuo Xu**, Minghong Wu, Mingnan Wang, Chenyuan Pan, Wenhui Qiu, Liang Tang, Gang Xu. Polybrominated diphenyl ethers (PBDEs) and hydroxylated PBDEs in human serum from Shanghai, China: a study on their presence and correlations. ***Environmental Science and Pollution Research*** 25 (2018) 3518-3526.

(5). ***Bentuo Xu**, Mohammad Boshir Ahmed, John L. Zhou, Ali Altaee, Minghong Wu, Gang Xu. Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanism, kinetics and controlling factors. ***Chemosphere*** 189 (2017) 717-729.

(6). **Bentuo Xu**, Minghong Wu, Chenyuan Pan, Yan Sun, Debao Yuan, Liang Tang, Gang Xu. Aquatic photolysis of hydroxylated polybromodiphenylethers under direct UV irradiation: a case study of 2'-HO-BDE-68. ***Environmental Science and Pollution Research*** 24 (2017) 14409-14416.

(7). **Bentuo Xu**, Gang Xu, Minghong Wu. Distribution and toxic effects of polybrominated diphenyl ethers (PBDEs) in organism. ***Journal of Shanghai University (Natural Science Edition)*** 23 (2017) 235-243.

Participation work:

(1). Minghong Wu, **Bentuo Xu**, Gang Xu*, Mingnan Wang, Jing Ma, Chenyuan Pan, Rui Sun, Tao Han, Liang Tang. Occurrence and profiles of polybrominated diphenyl ethers (PBDEs) in riverine sediments of Shanghai: a combinative study with human serum from the locals. ***Environmental Geochemical Health.*** 30 (2017) 729-738.

(2). Jianguo Sheng, Wenhui Qiu, **Bentuo Xu**, Hui Xu, Chong Tang. Monitoring of heavy metal levels in the major rivers and in residents' blood in Zhenjiang City, China, and assessment of heavy metal elimination via urine and sweat in humans. ***Environmental Science and Pollution Research.*** 11 (2016) 11034-11045.

(3). Chenyuan Pan, Ming Yang, Hai Xu, **Bentuo Xu**, Lihui Jiang, Minghong Wu, Tissue bioconcentration and effects of fluoxetine in zebrafish (*Daniorerio*) and red crucian cap (*Carassius auratus*) after short-term andlong-term exposure. ***Chemosphere.*** 205 (2018) 8-14.

(4). Minghong Wu, Chenyuan Pan, Ming Yang, **Bentuo Xu**, Xiangjie Lei, Jing Ma, Ling Cai, Jingsi Chen. Chemical analysis of fish bile extracts for monitoring endocrine disrupting chemical exposure in water: Bisphenol A, alkylphenols, and norethindrone. ***Environmental toxicology and chemistry.*** 35 (2016) 182-190.

(5). Gang Xu, Sihan Ma, Liang Tang, Rui Sun, Jiajia Xiang, **Bentuo Xu**, Yangyang Bao, Minghong Wu. Occurrence, fate, and risk assessment of selected endocrine disrupting chemicals in wastewater treatment plants and receiving river of Shanghai, China Chemosphere. ***Environmental Science and Pollution Research.*** 23 (2017) 25442-25450.

(6). Minghong Wu, Tao Han, Gang Xu, Chao Zang, Yijie Li, Rui Sun, **Bentuo Xu**, Yan Sun, Fenfen Chen, Liang Tang. Occurrence of Hexabromocyclododecane in soil and road dust from mixed-land-use areas of Shanghai, China, and its implications for human exposure. ***Science of the Total Environment.*** 559 (2016) 282-290.

(7). Minghong Wu, Jingcheng Pei, Ming Zheng, Liang Tang, Yangyang Bao, **Bentuo Xu**, Rui Sun, Yanfeng Sun, Gang Xu, Jianqiu Lei. Polybrominated diphenyl ethers (PBDEs) in soil and outdoor dust from a multi-functional area of Shanghai: Levels, compositional profiles and interrelationships. ***Chemosphere.*** 118 (2015) 87-95.

(8). Minghong Wu, Wenyan Shi, Peng Yuan, Xinhao Sheng, **Bentuo Xu**, Xiangxin He, Gang Xu, Jing Ma, Xiaoyong Deng, Ming Yang. Method of removing estrogen biological toxicity in water and device of electron beam radiation disposing water. ***Inventive patent.*** 2014100015401. (2016, authorized)

Publications made during the PhD candidature including articles not entirely related to the Thesis. Articles with asterisk marked were related to the thesis.

Awards

1. 2017 HDR Students Publication Award from Faculty of Engineering and Information Technology (FEIT), University of Technology Sydney (UTS) for publishing in high quality journals.

PhD Dissertation Abstract

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Thesis title: Photocatalysis of aqueous perfluorooctanoic acid by TiO_2 and Ga_2O_3 assisted with peroxymonosulfate under UV and visible light

Faculty: Faculty of Environmental and Information Technology

School: Civil and Environmental Engineering

Supervisors: Prof. Dr. John Zhou (Principal supervisor)

Dr. Ali Altaee (Co-supervisor)

Abstract

Perfluorooctanoic acid (PFOA) has attracted considerable attention worldwide due to its widespread occurrence and environmental impacts. However, a suitable technology for PFOA controlling is worthwhile to be investigated nowadays. This thesis studied the photocatalysis by different catalysts and found that Ga_2O_3 and TiO_2 had better performance for PFOA removal than CeO_2, In_2O_3 and CdS. In addition, Ga_2O_3 mixed with peroxymonosulfate (PMS) was investigated for the PFOA degradation under UV light. It showed excellent performance and that 100% of PFOA was degraded within 90 min and 60 min under 254 nm and 185 nm UV irradiation, respectively. PFOA in real wastewater exhibited similar degradation efficiency and 75-85% TOC was removed by Ga_2O_3/PMS under 254 nm UV irradiation. Thus, a good method with well degradation efficacy was established in this thesis for aqueous PFAS removal. Moreover, this thesis investigated the PFOA photodegradation by using powerful visible light (300 W, 829.6 mW cm^{-2}) in the presence of catalyst TiO_2 with PMS activation, which achieved 100% PFOA removal within 8 h. The presence of organic compounds in real wastewater

reduced the degradation efficacy of PFOA by 18-35% in Vis/TiO_2/PMS system. Therefore, PFOA could be controlled under no matter UV light or visible light by TiO_2/PMS system.

Gallium oxide (Ga_2O_3), titanium dioxide (TiO_2), cerium dioxide (CeO_2), indium oxide (In_2O_3), and cadmium sulfide (CdS) are commonly used under UV light as photocatalyst for the pollutants degradation. In this study, these five catalysts were applied for the photodegradation of PFOA and the performance decreases as: Ga_2O_3 > TiO_2 > CeO_2 > In_2O_3 > CdS. Notably, CdS had almost no capability for PFOA removal. The initial pH, quantum yield and band gap energy were used to explain the various catalytic ability among these catalysts. Significantly, the band gap energy decreases as: Ga_2O_3 > TiO_2 > CeO_2 > In_2O_3 > CdS, which exactly matched their degradation performance. Thus, band gap energy was significantly related to the photocatalytic ability for PFOA removal. Further, according to the scavenger experiments, photogenerated holes rather than electrons played the main roles in degrading PFOA by TiO_2, CeO_2 and In_2O_3. In comparison, photogenerated conduction band electrons were more important when photocatalysis was carried out with Ga_2O_3.

This research focused on the photocatalytic process for the treatment of PFOA in water by Ga_2O_3 and peroxymonosulfate (PMS) mixed directly in the PFOA solution under different light sources. The results showed excellent performance that 100% of PFOA was degraded within 90 min and 60 min under 254 nm and 185 nm UV irradiation, respectively. Moreover, the degradation efficacy was unaffected by initial PFOA concentration from 50 ng L^{-1} to 50 mg L^{-1}. Acidic solution (pH 3) improved the degradation process as high amount of PFOA was adsorbed on the surface of Ga_2O_3 via Coulombic attraction, leading to the promoted photocatalytic efficacy. The quantum yield in the PMS/Ga_2O_3 system under UV light (254 nm) was estimated to be 0.009 mol

Einstein^{-1}. Scavengers such as *tert*-butanol (*t*-BuOH), disodium ethylenediaminetetraacetate (EDTA-Na_2) and benzoquinone (BQ) were added into PFOA solution to assess the roles of sulfate radicals ($SO_4^{\bullet-}$), superoxide radical ($O_2^{\bullet-}$) and photogenerated electrons (e^-) as the active species with strong redox potentials for PFOA degradation in PMS/Ga_2O_3/UV system. Through the analysis of the intermediates, PFOA was degraded stepwise from long chain compound to shorter chain intermediates. In addition, PFOA in the real wastewater exhibited similar degradation efficiency and 75-85% TOC was removed by Ga_2O_3/PMS under 254 nm UV irradiation. Therefore, Ga_2O_3/PMS system was highly effective for PFOA photodegradation under UV irradiation, which has potential to be applied for the perfluoroalkyl substances (PFAS) treatment in water and wastewater.

This research also studied the PFOA photodegradation by using powerful visible light (300 W, 829.6 mW cm^{-2}) in the presence of catalyst TiO_2 with PMS activation. The addition of PMS induced a significant degradation of PFOA on TiO_2 under visible light compared with sole TiO_2 or PMS treatment. Under powerful visible light, 0.25 g L^{-1} TiO_2 and 0.75 g L^{-1} PMS in the solution at initial pH 3 was advantageous for the PFOA degradation, and achieved 100% PFOA removal within 8 h. Under UV light irradiation at 254 and 185 nm wavelength, TiO_2/PMS resulted in an excellent performance of almost 100% PFOA removal within 1.5 h, attributed to the high absorbance ability of UV light by the catalyst. The intermediates analysis showed that PFOA was degraded from long carbon chains to shorter chains in a stepwise manner. Furthermore, scavenger experiments indicate that $SO_4^{\bullet-}$ radicals from PMS and photogenerated holes from TiO_2 played an essential role in degrading PFOA. The presence of organic compounds in real wastewater reduced the degradation efficacy of PFOA by 18-35% in visible-TiO_2-PMS

system. In general, TiO_2-PMS could be an ideal and effective catalyst for the degradation of PFOA from wastewater using either visible or UV light source.

Keywords: Chemical bonds; Gallium oxide; Peroxymonosulfate; Photocatalysis; Perfluorooctanoic acid; Photogenerated electrons; Sulfate radicals; Visible light